

CLAIMS.

1. A metallocene catalyst system for producing polyolefins comprising:
 - A. a hafnocene-based catalyst component suitable for producing the high molecular weight fraction of the polyolefin;
 - B. one or more metallocene or post-metallocene components different from component A and suitable for producing the low molecular weight fraction of the polyolefin and wherein the metallocene catalyst component is unbridged;
 - C. an activating agent having a low or no co-ordinating capability and selected from borate, boronate or aluminate.
2. The metallocene catalyst system of claim 1 wherein the hafnocene-based component has a structure according to formula (I)



or according to formula (II)



wherein

- each Cp is a substituted or unsubstituted cyclopentadienyl ring;
- each R is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl or arylalkyl radical containing from 1 to 20 carbon atoms or two carbon atoms are joined together to form a C4-C6 ring;
- R'' is a structural bridge between two Cp rings;
- M is hafnium;

- Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl or arylalkyl radical having from 1 to 20 carbon atoms, a hydrocarboxy radical having from 1 to 20 carbon atoms or a halogen and can be the same or different from each other;
 - s is 0 or 1, g is 0, 1 or 2 and s is 0 when g is 0, n is 4 when s is 1 and n is 5 when s is 0,
 - X is an hetero atom ligand with one or two lone pair electrons and selected from the group VA or VIA, substituted or unsubstituted.
3. The metallocene catalyst system of claim 1 or claim 2 wherein the hafnocene-based component has at most two substituents on each cyclopentadienyl .
 4. The metallocene catalyst system of any one of claims 1 to 3 wherein the position of substituents on the hafnocene-based component is 3- and/or 5- for a cyclopentadienyl-type group, 3- and/or 6- for a fluorenyl-type group and 2- and/or 4- for an indenyl-type group.
 5. The metallocene catalyst system of any one of claims 1 to 4 wherein the bridge in the hafnocene-based catalyst component is Et or Me₂Si.
 6. The metallocene catalyst system of any one of claims 1 to 5 wherein Q in the hafnocene-based catalyst component is chlorine.
 7. The metallocene catalyst system of any one of claims 1 to 6 wherein X in the hafnocene-based catalyst component is nitrogen, phosphorus, oxygen or sulfur.
 8. The metallocene catalyst system of any one of claims 1 to 7 wherein the other one or more metallocene catalyst component is based on zirconium.

9. The metallocene catalyst system of any one of claims 1 to 8 wherein the other one or more metallocene catalyst component is substituted and has at least one bulky substituent.
10. The metallocene catalyst system of any one of claims 1 to 9 wherein the other one or more post-metallocene catalyst component is an iron complex of the 2,6-bis(imino)pyridyl ligand.
11. The metallocene catalyst system of any one of claims 1 to 10 further comprising a cocatalyst.
12. The metallocene catalyst system of any one of claims 1 to 11 wherein the additional cocatalyst is an aluminium alkyl.
13. The metallocene catalyst system of any one of claims 1 to 12 further comprising an inert inorganic support.
14. The metallocene catalyst system according to any one of claims 1 to 13 wherein the inorganic support is silica having a specific surface area of from 200 to 700 m²/g and a pore volume of from 0.5 to 3 ml/g.
15. A process for preparing the catalyst system of any one of claims 1 to 14 comprising the steps of
 - A. providing a first hafnocene-based metallocene catalyst component suitable for producing the high molecular weight fraction of the polyolefin;
 - B. providing one or more metallocene or post-metallocene catalyst components different from the component of step A and suitable for producing the low molecular weight fraction of the polyolefin wherein the metallocene catalyst component is unbridged;

- C. activating the metallocene components with an activating agent having an ionising action and a low or no co-ordinating capability selected from borate, boronate or aluminate;
- D. optionally immobilising the catalyst system on an inorganic support.

16. A process for preparing polyolefins comprising the steps of:

- a. selecting a catalyst system according to any one of claims 1 to 14;
- b. optionally providing a cocatalyst;
- c. introducing the catalyst system and optional cocatalyst into a polymerisation zone containing an olefin monomer and an optional co-monomer and maintaining the reaction zone under polymerisation conditions;
- d. extracting the desired polyolefin.

17. The process of claim 16 comprising the additional step of pre-polymerisation prior to polymerisation step c).

18. The process of claim 16 or claim 17 wherein the polyolefin is polyethylene or polypropylene.

19. Use of the catalyst system according to any one of claims 1 to 14 to produce polyolefins wherein the molecular weight of the high molecular weight fraction is between 5 times and 15 times larger than the molecular weight of the low molecular weight fraction and preferably is about 10 times larger than the molecular weight of the low molecular weight fraction.

20. Polyolefins obtainable by the process of any one of claims 16 to 19, having the molecular weight of the high molecular weight fraction about 10 times larger than the molecular weight of the low molecular weight fraction.